

SCIENCE FOR CERAMIC PRODUCTION

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PROCESSES OCCURRING DURING PLASMA-CHEMICAL SYNTHESIS OF REFRACTORY SILICATE MATERIALS

N. K. Skripnikova,¹ V. I. Otmakhov,² and O. G. Volokitin¹Translated from *Steklo i Keramika*, No. 1, pp. 19–21, January, 2010.

The processes occurring during plasma-chemical synthesis of melts from silicate-containing materials as well as technological regimes during the production of silicate refractory melts using highly concentrated heat flows are examined. The results of physical – chemical studies of the initial silicate materials (basalt, oil shale wastes, and ash) and aluminosilicate glasses obtained are presented.

Key words: plasma-chemical synthesis, melts, silicate-containing materials, highly concentrated heat flows, aluminosilicate glasses.

The production of melt from refractory silicate-containing materials for the production of mineral fibers using conventional technologies entails large energy consumption, and sometimes it is practically impossible because the melting temperatures of the initial materials are so high. To solve this problem it is proposed that the energy from low-temperature plasma be used to produce silicate melt.

The objective of the present work is to investigate the processes occurring in a plasma-chemical reactor during the production of silicate melt.

Basaltic rock from a deposit in the Kemerovo Oblast', oil shale wastes, and ash from a central heat-and-power plant in Seversk (Tomsk Oblast') were used as the initial materials to obtain melts. The chemical composition of the initial materials is presented in Table 1. As one can see, all the initial materials used contain a considerable amount of SiO₂ (49–61%), which is the main glass former.

The initial materials were melted in a plasma facility (RF patent declaration No. 2007123894). The technological regimes were as follows: $U = 160$ V, $I = 220$ A, $P = 35$ kW, $q = 1.8 \times 10^6$ W/m². The principle of operation of the facility is based on the interaction of highly concentrated plasma flows with powdered refractory silicate-containing material (basalt, oil shale wastes, ash), as a result of which the disperse particles are heated and a homogeneous melt is obtained [1].

The plasma-chemical processes resulting in the formation of silicate melt differ from the classical processes by the nonequilibrium state and rate of flow. This is explained by the temperature which is developed in the plasma-chemical reactor (3000–5000 K) when melt is produced. All silicate and glass formation processes proceed in a single stage. The chemical composition of the initial material changes in the course of melt formation; melting and vaporization processes also occur at rates determined by the ratio of the heat flux and the energy required for the phase transition. As a result of these transitions the silicate melts become enriched with multivalent cations Si, Al, Fe, and Ca [2], as chemical analysis of the aluminosilicate glasses obtained shows (see Table 1).

Intense vaporization of the components of the initial materials can be expected at the melting stage; the rate of vaporization increases with increasing temperature: low-melting — with subsequent dissociation to atoms and refractory — to unstable oxides.

Physical – chemical studies — x-ray phase analysis and IR spectrometric analysis — were performed to determine the processes occurring during high-temperature synthesis of the melts.

The results of the XPA for the materials studied are presented in Fig. 1. As one can see, the main phases for basalt are quartz ($d = 4.74, 3.67, 1.82$ Å), aluminosilicate compounds ($d = 3.23$ and 2.96 Å), and pyroxene ($d = 2.53$ and 2.015 Å). In the case of oil shale wastes, together with the main phase of quartz ($d = 5.15, 4.52, 3.81, \text{ and } 1.82$ Å)

¹ Tomsk State Architectural and Construction University, Tomsk, Russia.

² Tomsk State University, Tomsk, Russia.

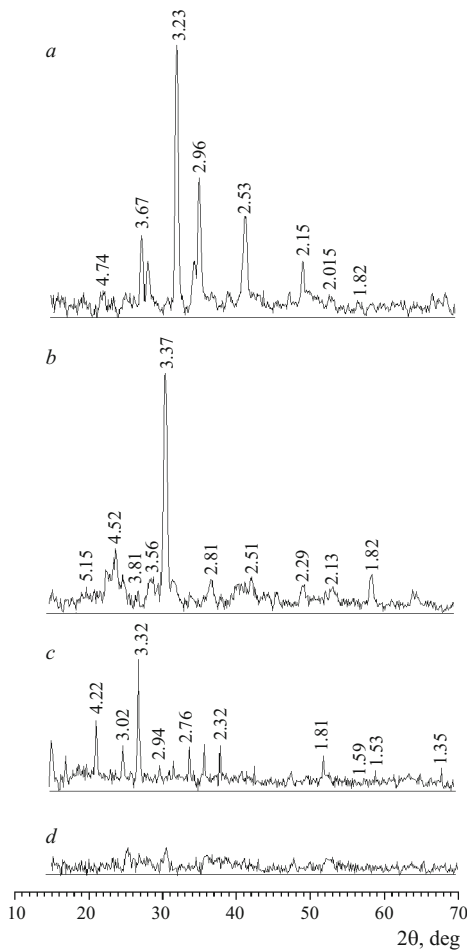


Fig. 1. X-ray diffraction patterns of the materials investigated: *a*) basalt before melting; *b*) oil shale wastes before melting; *c*) ash before melting; *d*) all materials after melting.

phases of aluminosilicate compounds ($d = 3.37$, 2.81 , and 2.51 Å) as well as wollastonite ($d = 3.56$ Å), diopside ($d = 2.29$ Å), and anortite ($d = 2.13$ Å) are also present. For ash the main phases are quartz ($d = 3.32$, 3.02 , and 2.76 Å), aluminosilicate anortite-like ($d = 2.94$ and 1.53 Å), and wollastonite-like ($d = 1.81$, 1.59 , and 1.35 Å) compounds,

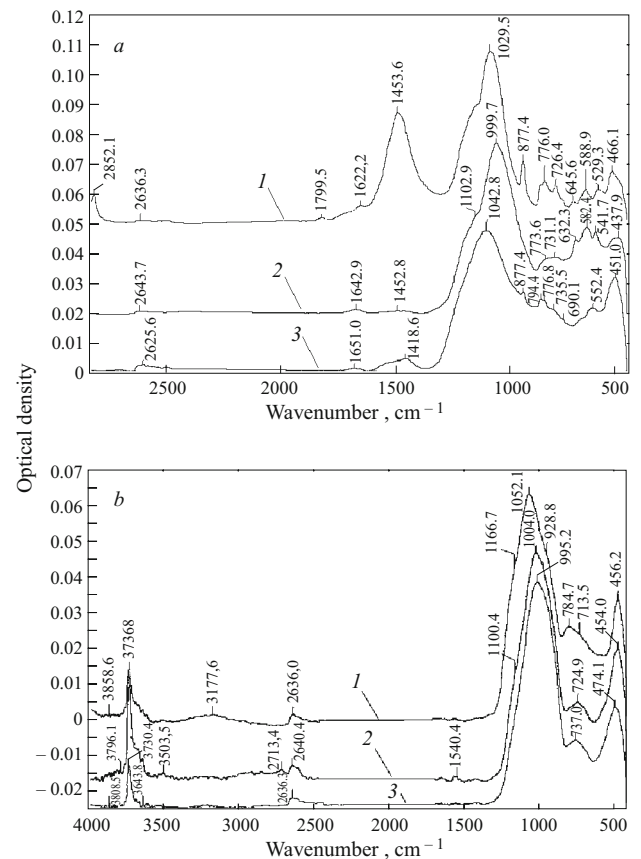


Fig. 2. IR absorption spectra of the initial material (*a*) and aluminosilicate glasses (*b*), obtained from ash from a central heat-and-power plant (1), oil shale wastes (2), and basalt (3).

pyroxene ($d = 4.22$ Å), and a glass phase. For all materials, after melting there are no characteristic peaks, which indicates the absence of crystal structure, i.e., the melts of all materials after cooling are x-ray amorphous.

IR spectroscopic analysis of the materials was performed before and after melting. The IR spectra were obtained with a Nicolet 6700 IR-Fourier spectrometer (Thermo Nicolet Co.).

Figure 2*a* shows the IR absorption spectra of the initial materials from which aluminosilicate glasses were obtained.

TABLE 1.

Materials	Content, wt. %					
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	other
<i>Initial materials</i>						
Basalt	49.40	16.17	7.24	8.98	3.37	14.84
Oil shale wastes	61.59	23.36	7.91	1.60	1.27	4.27
Ash from central heat-and-power plant	51.16	34.57	3.62	8.33	0.91	1.41
<i>Aluminosilicate glasses obtained</i>						
Basalt	52.9 ± 5.0	19.9 ± 2.0	9.8 ± 1.0	10.9 ± 1.0	6.5 ± 0.5	± 9.5
Oil shale wastes	61.1 ± 6.0	26.0 ± 2.5	8.5 ± 1.0	2.1 ± 0.2	2.3 ± 0.2	± 9.9
Ash from central heat-and-power plant	64.6 ± 6.5	23.0 ± 2.3	5.4 ± 0.5	4.7 ± 0.5	2.3 ± 0.2	± 10.1

It is evident that all spectra of the initial materials contain a wide absorption band with a maximum at 999.7 cm^{-1} for basalts, 1029.5 cm^{-1} for oil shale wastes, and 1042.8 cm^{-1} for ash from a central heat-and-power plant. This band is due to stretching vibrations of Si – O – Si bonds. The wide intense absorption band with a maximum at 1453.6 cm^{-1} for the oil shale wastes can be attributed to the vibration of the hydroxyl group OH^- [3] of a disordered form of kaolinite $[\text{Al}_{1.8}\text{Fe}_{0.1}\text{Mg}_{0.1}]\text{S}_2\text{O}_5(\text{OH})_4$, which can appear in the form of a clayey component in this mineral. All other discrete absorption bands are due to the deformation vibrations of the Si – O – Si bond, vibrations of the silicon-oxygen tetrahedra, and vibrations of the Al – O – Al bond for different forms of Al_2O_3 which are present in different polyamorphous modifications.

Figure 2b shows the IR spectra of the glasses obtained. Superficially, the IR spectra should be referred to aluminosilicate glasses with different degrees of ordering of the polymer framework of the glass. The main absorption bands 995.2 cm^{-1} for basalt glass, 1004.0 cm^{-1} for glass from oil shale wastes, and 1052.1 cm^{-1} for glasses from ash from a central heat-and-power plant are due to the vibrations of the Si – O – Si bond. The position of this band depends strongly on the content of glass-forming cations whose chemical bond with oxygen has a substantial covalent component and which participate with silicon-oxygen tetrahedra in the formation of the spectra of internal vibrations of a mixed polyanion. The absorption bands at 737.0 , 724.9 , and 784.7 cm^{-1} are due to deformation vibrations of the Si – O – Si bond and those at 474.1 , 454.9 , and 455.2 cm^{-1} are due to the vibrations of the silicon-oxygen tetrahedron.

The most ordered glasses are those obtained from the heat-and-power plant ash, since the maximum of the absorption band for a stretching vibration of the bond 1052.1 cm^{-1} is closest to the analogous maximum of the absorption band of quartz glass, which is the most ordered polymer structure. Melts and glasses contain pre-embryonic nanoparticles, for which the same chemical bonds as in the initial materials are characteristic. On this basis it can be expected that during

melting of the initial materials crystals of aluminosilicate compounds are formed in the melt, but they are still so small that they are not visible in the x-ray diffraction pattern. The glasses obtained are amorphous only in a thin, rapidly cooled, surface layer.

In summary, the technology for obtaining silicate melt from basalt, oil shale wastes, and ash using the energy from a low-temperature plasma permits synthesizing aluminosilicate glasses with different degrees of ordering. The degree of ordering increases in the following order: aluminosilicate glass from heat-and-power plant ash, oil shale wastes, and basalt.

Therefore, mineral wool and articles based on it with high physical – mechanical and heat-engineering properties, possessing high performance characteristics (chemical, heat, and water resistant) and longevity, can be fabricated from aluminosilicate melt obtained by the plasma-chemical method and sprayed into fibers. This is due to the content in aluminosilicate glass of SiO_2 (52 – 64%) and Al_2O_3 (19 – 26%) which affect the pH (7 – 10) of the mineral fiber obtained.

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